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Biopolymer as Reinforcement into Natural Matrices: a New Route to Bio-Composite Materials

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1. Introduction

In order to design a new, efficient and competitive material, no process is better than combining several components, and their own performance. Such composite materials are designed to meet specific technical expectations. They mostly consist in an organic, ceramic or metallic reinforced matrix, where reinforcement can be long or divided fibres, divided particles, filling dust... Reinforcement is expected to confer to the material its mechanical properties. The matrix binds the reinforcement parts together and guaranties the forces transmission.

Within the composite materials widely manufactured in mass industrial production, an attractive and well-known, tremendously emerging composite category is the WPC, or Wood Plastic Composites category. This material is composed of a polymeric matrix, preferably thermoplast resin as polyvinylchloride or polyethylene, even if thermoset resins as epoxies or phenolics can be, or have been, used (phenol-formaldehyde mixed with wood flour known as Bakelite, for instance). The reinforcement has to be a natural compound as wood or possibly other fibrous biomass. The addition of fillers leads to two major improvements. First the material is lightened, as fillers density is lower than the matrix density. Second, the mechanical properties are expected to be improved.

Literature content is abundant as the combinations potential is huge. Most of times, the admixtures encounter a poor interfacial adhesion between natural hydrophilic polar fillers and synthetic hydrophobic nonpolar matrix. To reach a better interfacial cohesion, chemical treatment of the surface of reinforcing components has to be carried out to allow creating bridge of chemical bonds between matrix and reinforcement. Bledzki & Gassan, 1999 and George et al., 2001 provide a list of possible cellulosic fibers treatments from esterification or acetylation of cellulose to treatment with isocyanates or silanes or use of triazine or organosilanes as coupling agents.

The use of cellulosic fibres instead of synthetic reinforcements allows to reduce production cost but also to involve natural compounds within the material conception. In the same guideline, biobased polymers have been more recently considered as matrices. Those biopolymers come from bioresources and/or can be degraded at the end of their life cycle. Bio-

sourced bio-polymers can come from animals (chitin, protein, ...), microorganisms (poly(lactic acid), poly(hydroxyalkanoates), ...), or plants (starch, cellulose, lignin, ...). Fossil bio-polymers are mostly composed of polycaprolactone, poly(lactic acid), poly(glycolic acid), polyvinylalcohol and polyesteramide. Bio-polymers are competitive with standard polymers in terms of performance, even if their producing cost and involved energy consumption are still high.

In the environmental point of view, entirely biobased composites are obviously promising. Reinforcement of biopolymer matrices with natural fibres or fillers has been reported. Fink & Ganster, 2006 witnessed a good compatibility between cellulosic fibres with poly(lactic acid) without coupling, while polyethylene, polypropylene and polystyrene had to be grafted or copolymerised with maleic acid anhydride. Gatenholm et al., 1992 noticed also an excellent dispersibility of cellulose fibres in polyhydroxybutyrate (PHB) matrix compared with synthetic matrices.

Bio-based, natural materials are often sensitive to their environment. It is the case of wood, used since centuries in the building, furniture, artistic fields for its excellent properties. Constituted of cellulose reinforcement in a ligneous matrix, wood is itself a natural composite. But its high hydrophilic character and sensitivity to biological attacks are its most limiting disadvantages. Indeed, wood exposed outdoor has to be protected either by surface coatings or preservation chemicals. Coatings have the advantage to be more or less innocuous to the environment, but a mechanical crack in the coating layer leads to unavoidable and irreversible wood degradation. Chemical treatments penetrate the wood structure in a higher thickness, but a major concern is the releasing of preservative chemical in the environment. That's why grafting or in-situ polymerization of chemical compounds is expected. Rowell, 2005 described the chemical modification of wood. As hydroxyl groups in wood are responsible of the hydrophilic property, their esterification with acid anhydrides is a possibility to reduce moisture affinity with wood. Different epoxydes or isocyanates are also susceptible to react with wood. Wood impregnation by polyethylene glycol, polyglycerols, formaldehyde resins, styrenes or methyl methacrylate have been widely reported (Ibach & Rowell, 2001; Zhang et al., 2006).

A different way to produce an entirely biobased composite is to reinforce a natural matrix, as wood, with natural or biodegradable polymers, as polymerized lactic acid. This association has not been much reported to date (Noël et al., 2009). The affinity between both materials should lead to interesting chemical reaction providing wood protection. Grafting of carboxylic end groups of poly(lactic acid) onto hydroxyl groups of wood, and in-situ polymerization should avoid any chemical release in the environment. What is looked for is an increase in wood dimensional stability and biological resistance. Simultaneously, the density increase due to the treatment is expected to induce gainful property variation.

2. Composite material manufacturing

2.1 Method

Poly(lactic acid) (PLA) is one of the most produced and processed bio-polymers. It is produced from lactic acid monomers polycondensation. Lactic acid can be synthesized from fossil resources or extracted from corn and produced by biotechnological means, which gives the natural origin of PLA. Polycondensation of aqueous lactic acid into PLA is mostly achieved by Ring Opening Polymerization (ROP): the first step is a direct polycondensation leading to oligomers. This step is limited by a complicated elimination of the water produced. In the second step, the oligomers are depolymerized into lactide cycles. The last

step consists in opening the cycles to build long PLA polymer chains. Residual monomers which did not react are then recycled and reused. The only first step of direct polycondensation has been considered to prepare the wood treatment product.

Solid wood impregnation can be achieved in two steps. The first step consists in making the acid treatment penetrate the cells. This is achieved under vacuum. The second step consists in making the acid mono- and/or oligomers polymerize into the wood matrix.

To help polymerization, aqueous acid dilution must be first dehydrated and oligomerized. Indeed, water would be an obstacle to the in-situ polymerization step. On the other side, if oligomerization can help the in-situ polymerization step, attention must be paid to the oligomers viscosity, as the perfect case would be to achieve not only the lumen but also the cell wall penetration. It has been shown that an oligomerization of aqueous lactic acid (88% in water), leading to a mean polymerization degree of 2 to 3, is a good compromise. Such a product possesses a viscosity of 750 cP, and can be obtained by vacuum dehydration at 120°C for 1 hour. This gives stable oligomers, which can be stored in close flasks at room temperature for several weeks.

Wood matrix must be dried until anhydrous state before the impregnation step. Removing as much water molecules as possible is also necessary to free the hydroxyle grafting sites. Samples of pine sapwood (*Pinus sylvestris*) and beech (*Fagus sylvatica*) are used as reference species.

The impregnation process begins with a vacuum step where most of the air contained in wood is extracted. Then, lactic acid oligomers are introduced in the container until covering wood samples. The container stays some hours in low pressure. Alternation of low and atmospheric pressure is conducted for one day. This process is expected to allow most of the air contained in wood to be replaced by oligomers. The chemical affinity between oligomers and wood constituents in the cell walls leads then to the wall penetration.

Following this protocol, high impregnation yields can be reached. Indeed, up to 70 % of mass uptake is noticed on beech and 120 % on pine sapwood. According to wood and lignocellulosics mean densities, and following the simplified formula (1), it seems that up to 80 % of wood cellular vacuum (beech and pine sapwood respectively) can be filled with oligomers. This is information of a quite good affinity between lactic acid oligomers and solid wood.

$$P(\%) = \left(1 - \frac{\rho_0}{\rho_{lcm}}\right) \times 100 \quad (1)$$

with P : wood porosity

ρ_0 : anhydrous wood density

ρ_{lcm} lignocellulosic material density $\approx 1530 \text{ kg.m}^{-3}$

Lactic acid oligomers final polymerization is then achieved by oven-heating. Checking the impregnation yield evolution along heating time gives valuable information about the in-situ polymerization rate. Indeed, water is the polycondensation by-product gradually eliminated.

2.2 Alternatives

The role of lactic acid polymers into wood is to reinforce the lignocellulosic matrix. Therefore, the favourite polymerization protocol is the one which leads to the highest in-situ polymerization degree.

In the polymers manufacturing industry, especially PLA manufacturing, designing a polymer with a significant polymerization degree in an efficient process makes the use of chemical catalysts unavoidable.

As care must be taken not to expose wood to severe temperature, catalyst addition is a possibility to help polymerization in soft conditions. A lot of well suited chemical catalysts can be found in the literature. The assumption of their efficiency is done by dispersing them separately into the oligomers, without being impregnated into the wood matrix. The as-prepared mixtures are vacuum heated and their polymerization degree assessed. Sulfuric acid and Tin (II) ethyloxanoate have proved themselves to be the most efficient catalysts. Indeed, starting from the oligomers product, a second heating step leads to a polymerization degree of 40 with 0.6% sulphuric acid (120°C / 1h) and 24 with 5% Tin (II) ethyloxanoate (150°C / 1h).

A commercially available PLA shows a density of around 70'000 g.mol⁻¹. Because of physical restrictions, this is obviously not achievable into the lignocellulosic matrix. All the more that polymerization conditions have to be soft enough to avoid wood degradation.

Following the in-situ polymerization by mean of Thermo-Mechanical Analysis (TMA) gives valuable information about the influence of the components the ones on the others. Impregnated beech samples (20mm longitudinal x 0.6mm radial x 5mm tangential) have sustained a three points bending test within a temperature increase of 200 °C (from 25 to 225°C with a rate of 2°C.mn⁻¹). As can be seen in Figures 1 and 2, a critical temperature of about 112°C induces a significant decrease of the Young Modulus.

In the same temperature range (from around 60°C to around 112°C), the Young Modulus decrease is related to a strong deformation. This is due to the oligomers viscosity decrease, which leads to a deeper penetration in the matrix. This is translated by a noticeable wood softening. From 112°C to around 180°C, Young Modulus increases, while deformation is reduced. This is due to the oligomers polymerization which reinforces the structure.

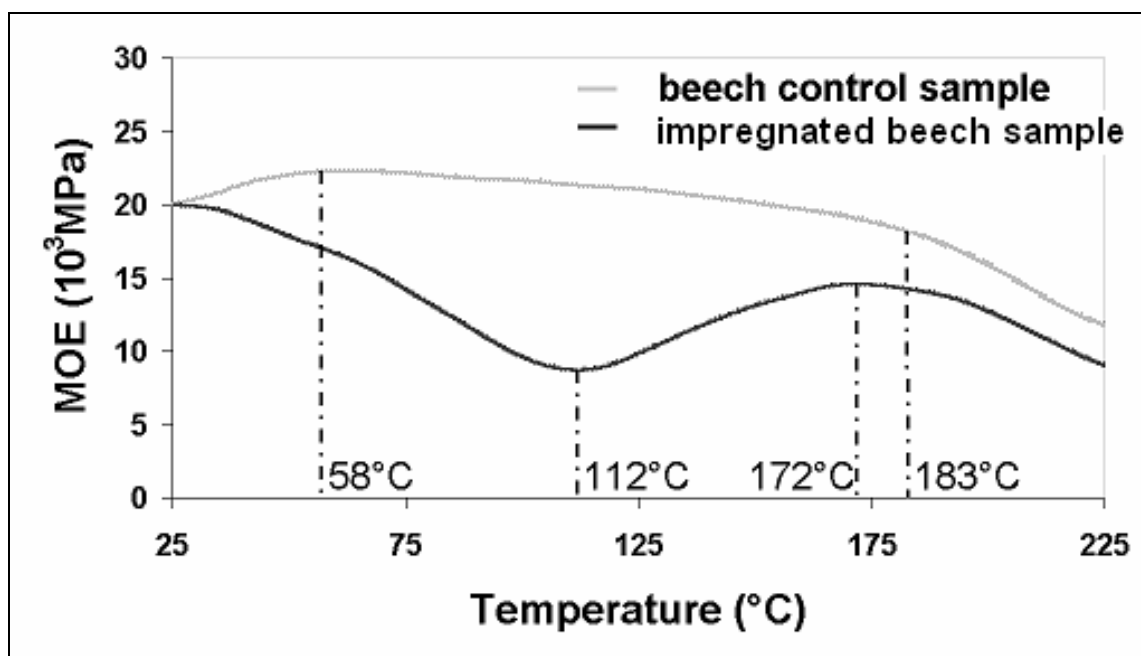


Fig. 1. Young's modulus behaviour of impregnated beech veneer sample compared to beech control sample

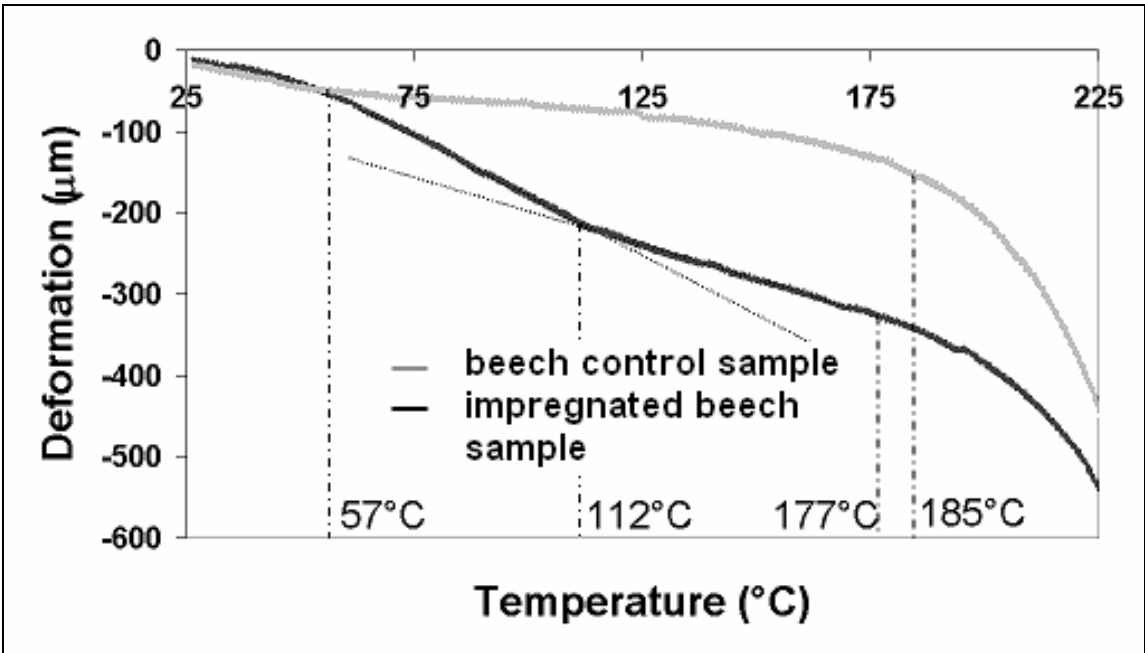


Fig. 2. Deformation of impregnated beech veneer sample compared to beech control sample
To focus on the softening temperature, TMA bending tests have been carried out under five isothermal conditions (Figure 3). This reveals that from 120°C, the first Young Modulus strong decrease step is followed by a compensating increase step.

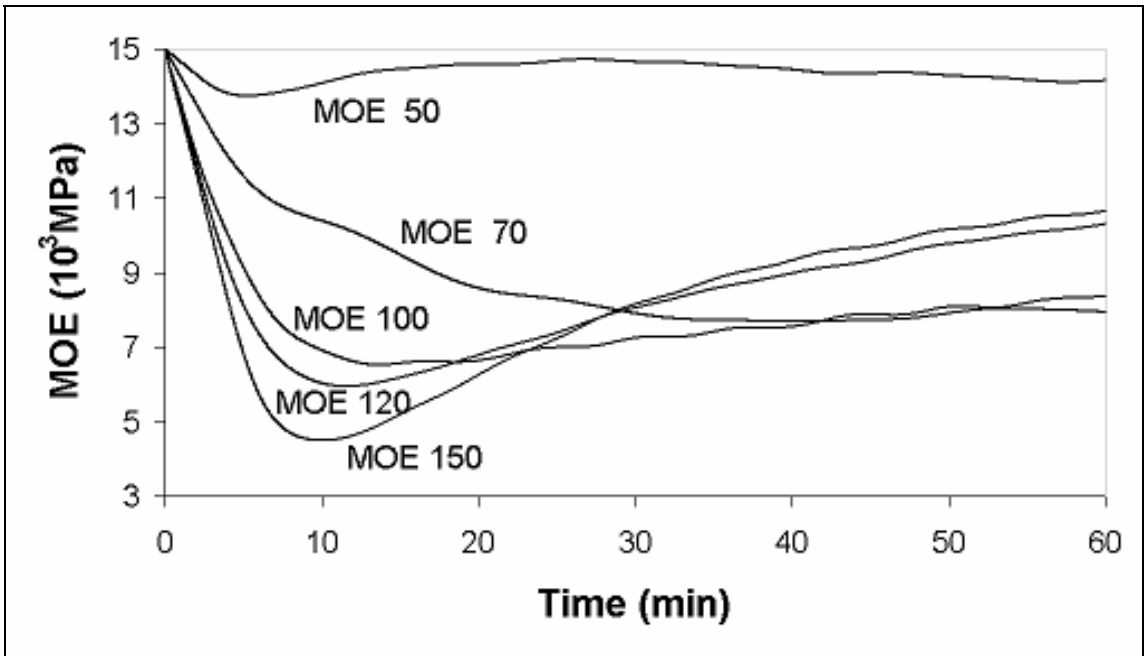


Fig. 3. Young's modulus behaviour of impregnated beech veneer samples subjected to isothermal conditions at 50, 70, 100, 120 and 150 °C
On the basis of these observations, the treatment process has been set up (Figure 4).

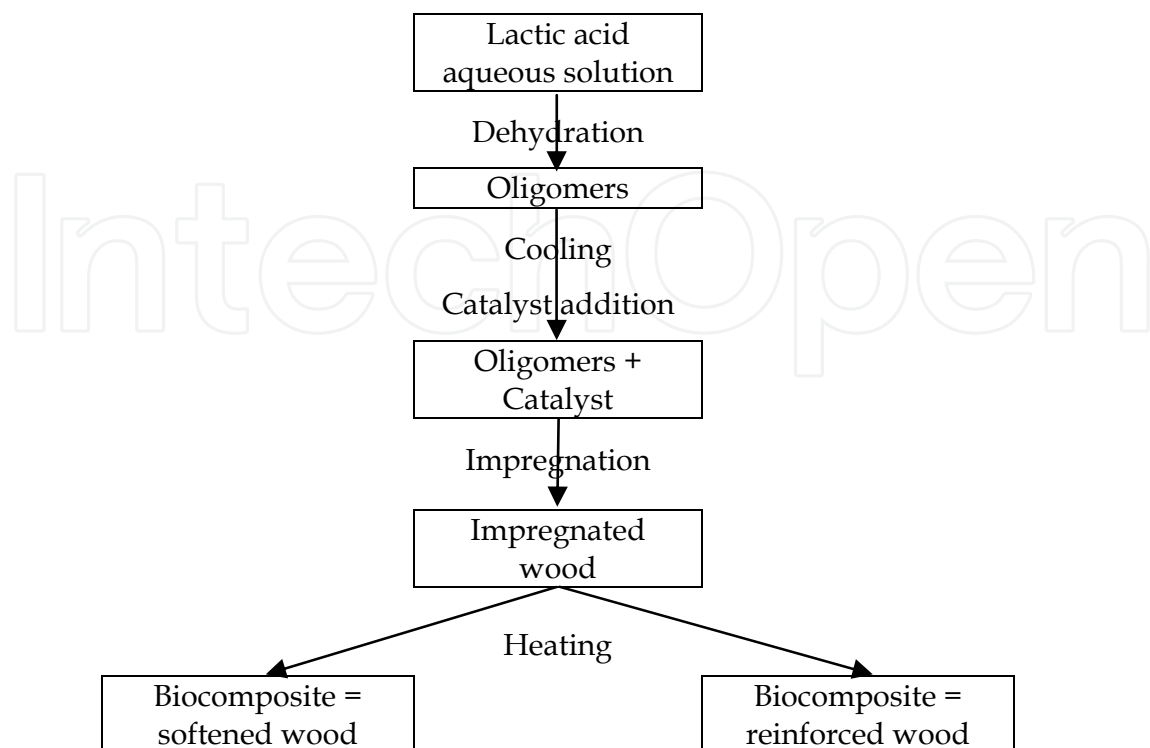


Fig. 4. Composite manufacture processing

2.3 Physical observation

Treatment has been conducted on samples in a macroscopic scale. A strong interaction between wood and the polymerized oligomers can be attested.

The composite material obtained by mean of the short treatment without catalyst consists in impregnated wood, partially dry. No grafting or strong polymerization seems to have occurred. The long treatment induces a complete drying.

Obtained by mean of catalyzed short treatment, the material obtained is strongly softened, partially dry and highly darkened. Completely dry after the long treatment, the composite appears hard and brittle.

A strong swelling is noticed after heating step: up to 30%. As oligomers impregnation induces only 2% swelling, this indicates that oligomers inside wood lumens penetrate the cell walls during heating step. Figure 5 shows a transverse section of long treated pine where lumens appear empty.

Chemical catalysis causes another physical reaction: a strong darkening of wood during heating step. According to Formula (2), figure 6 shows the ΔE^* of pine sapwood and beech samples due to heating.

$$\Delta E^* = \sqrt{(L_f^* - L_i^*)^2 + (a_f^* - a_i^*)^2 + (b_f^* - b_i^*)^2} \quad (2)$$

with L^* , a^* and b^* the three colour coordinates in the CIELab system of samples before (i=initial) and after (f=final) treatment.

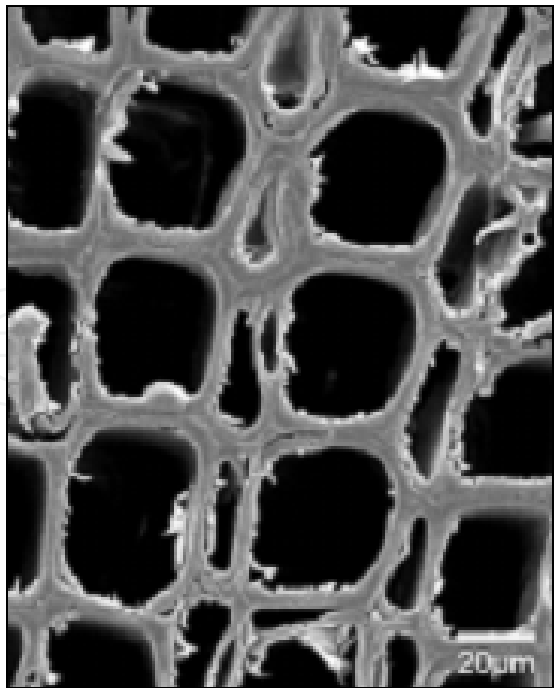


Fig. 5. SEM micrographs of treated pine sapwood sample

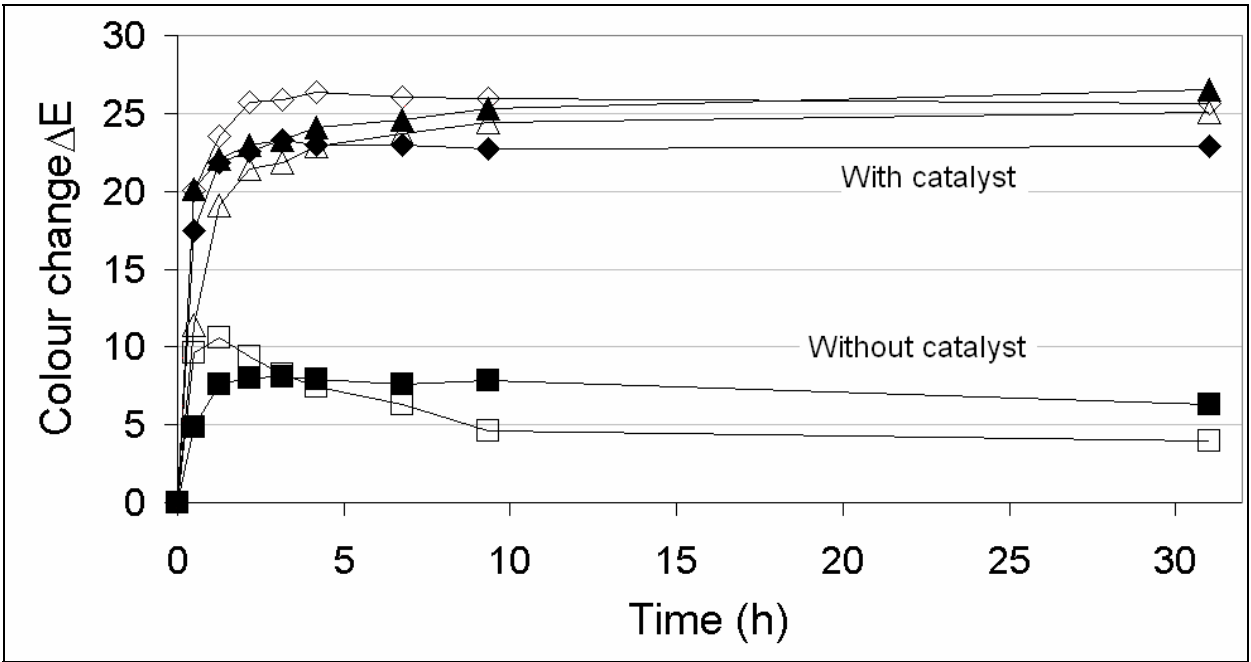


Fig. 6. Colour change of treated samples during the heating period

Colour change of samples treated without catalyst is in the range of classical colour changes due to heat treatment on wood. With catalyst, darkening is strong enough to modified wood appearance.

PLA darkening while processing is often reported in the literature. PLA purity, related to the L-isomers content is considered as one possible reason of coloration. But interactions between oligomers and lignocellulosic compounds could also lead to such a darkening. Every constituent of the composite has been subjected to short and long heating: oligomers,

wood, cellulose, extracted wood, extractives, and lignin sulfonate powder. Darkening is observed on wood subjected to short and long catalysed treatment, on low purity oligomers subjected to sulphuric acid catalysed long treatment, on cellulose subjected to catalysed long treatment, on extractives subjected to sulphuric acid catalysed treatment. Lignin sulfonate powder, already brown, is strongly darkened in every case.

Wood softening is translated by the wood structure disintegration into single fibres. Middle lamella, mostly composed of lignin, seems to be destroyed by the chemical treatment and do not fix cells anymore. Figure 7 attests this observation.



Fig. 7. Treated pine sapwood whose tracheids are easily manually disjoined

Softening and darkening are strongly related and both phenomenons imply a lignin modification.

3. Product performance

3.1 Physico-chemical properties

In-situ polymerization of lactic acid oligomers has been analysed by FTIR spectroscopy and gel permeation chromatography.

Infra-red spectroscopy attests the occurrence of polymerised lactic acid into wood structure (Figure 8). Indeed, PLA characteristic peaks at 875 cm^{-1} and 765 cm^{-1} are superimposed on wood spectra, and the shift of carbonyl absorption band from 1746 to 1764 cm^{-1} during heating indicates a higher ester linkage content.

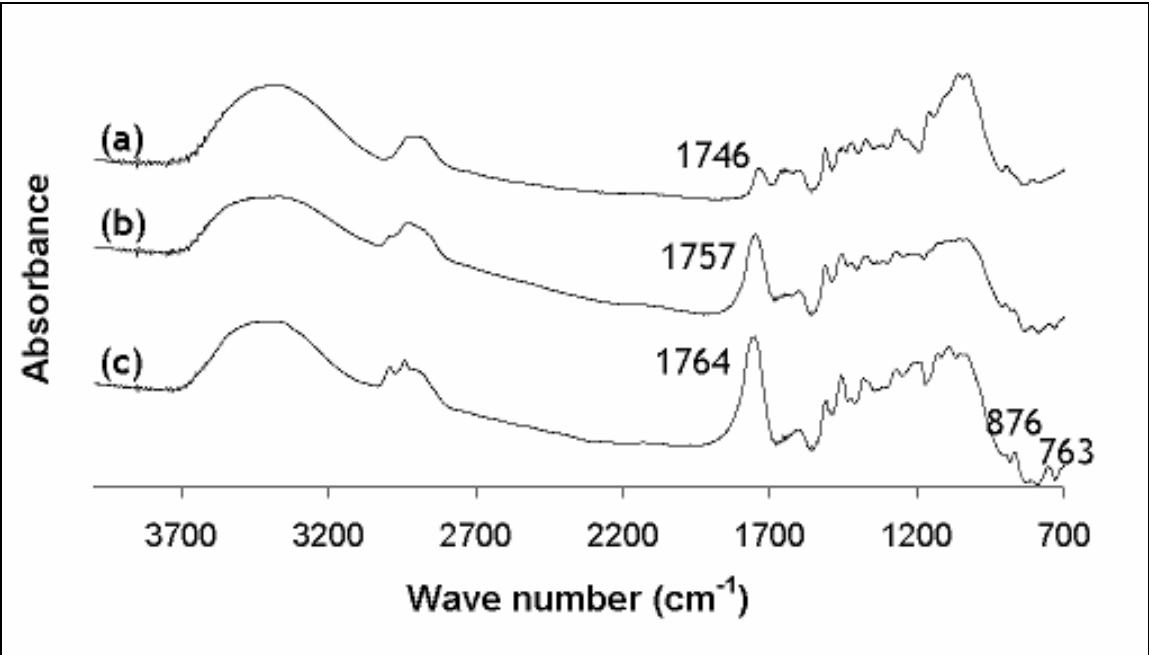


Fig. 8. FTIR spectra of pine control sample (a), pine after catalysed short (b) and long (c) treatment

Polymer extracted from treated samples by chloroform show a noticeable increase and a strong enlargement in molecular weight distribution (Figure 9).

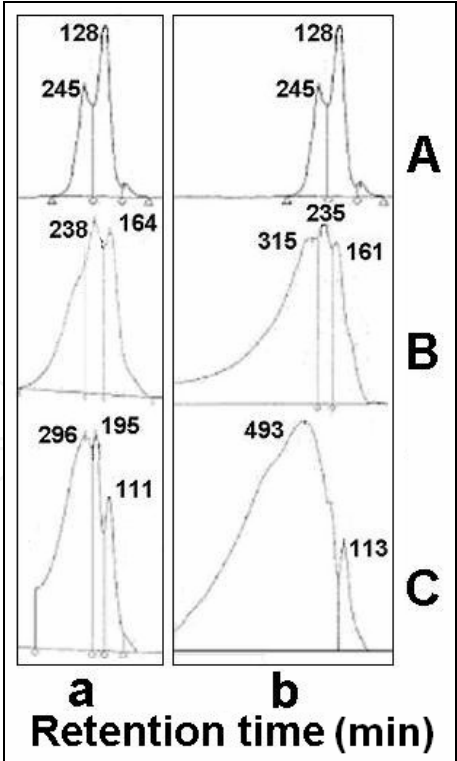


Fig. 9. GPC chromatograms of impregnated oligomers (A), oligomers extracted from short (B) non catalysed (a) and catalysed (b) treatment, and oligomers extracted from long (C) non catalysed (a) and catalysed (b) treatment

After short treatment, oligomers are not durably linked to the wood structure as around 90% weight loss by chloroform extraction is noticed. No characteristic oligomer peaks is noticed in the FTIR spectra neither. After long treatment, around 50% weight loss indicates that half the amount of oligomers remained in wood, either due to physical trapping of the molecules or hydrogen bondings.

3.2 Physical performance

Expected to be used outside, wood has to reach a suitable performance according to swelling. The anti-swelling efficiency of long treated samples has been evaluated around 70%. Even samples subjected to water leaching, which is susceptible to occur in the environment, show the same anti-swelling efficiency values. This is due to the occurrence of oligomers into the cell walls, around cellulose microfibrils where water uptake takes usually place, and promises a good outside stability. Water leaching has been quantified as around 16% oligomers weight loss on the oligomer content basis, after one week of leaching. It has been found that acid concentration of removed water increases in time along with the gradual hydrolysis of lactic acid chains in the wood cell walls.

3.3 Mechanical performance

Mechanical performance have been assessed in terms of bending strength (σ_B), compression strength (σ_C), shearing strength (f_v), and hardness (Brinell HB and Monnin N normalized methods). Table 1 summarizes densified samples strengths.

Specimen	σ_B (MPa)	σ_C (MPa)	f_v (MPa)	N
Beech control	120	72		11.9
Non catalysed treatment	142	97		15.3
Sulfuric acid catalysed treatment	50	107		19.4
Tin octoate catalysed treatment	86	92		19.3
Pine sapwood control	170	47	2.7	3.7
Non catalysed treatment	146	66	2.2	3.3
Sulfuric acid catalysed treatment	172	64	1.1	7.8
Tin octoate catalysed treatment	181	54	1.2	5.2

Table 1. Mechanical properties of densified composite

Densified composite shows a different mechanical behaviour according to the species and treatment.

Pine samples bending strength is not affected by catalysed or non catalysed treatment. Contrariwise, catalysed treatments strongly affect beech samples. With every treatment on both species, the bending deflection is decreased, which translates the brittleness of the material. This is not necessarily a limitation. Especially in the case of pine samples, where the same bending force leads to break but with less deformation.

Compression strength parallel to the grain is increased by every treatment on both species, with reduced deflection as well.

Shearing strength test performed on pine samples confirms a strong embrittlement of middle lamella. Indeed, shearing strength is strongly decreased by catalysed treatments. Monnin hardness is strongly increased by catalysed treatment.

Densified composite obtained by non catalysed treatment shows improved or at least unchanged mechanical properties.

Densified composite obtained by catalysed treatment shows improved compression strength and Monnin hardness, but an obvious degradation of fibres cohesion has occurred.

Mechanical assessment of softened composite has been used to quantify the structural degradation. Table 2 summarizes softened samples strengths.

Specimen	σ_B (MPa)	f_v (MPa)	N
Beech control	120		11.9
Non catalysed treatment	77		2.7
Sulfuric acid catalysed treatment	15		5.3
Tin octoate catalysed treatment	6		1.5
Pine sapwood control	170	2.7	3.7
Non catalysed treatment	75	2.3	0.3
Sulfuric acid catalysed treatment	14	1.1	1.8
Tin octoate catalysed treatment	28	101	1.3

Table 2. Mechanical properties of softened composite

Compression strength cannot be assessed on softened samples because no breaking point is ever reached (Figure 10). Instead, crushing happens progressively along the test. Bending strength, shearing strength and hardness are strongly decreased by every treatment, even more by catalysed treatments.

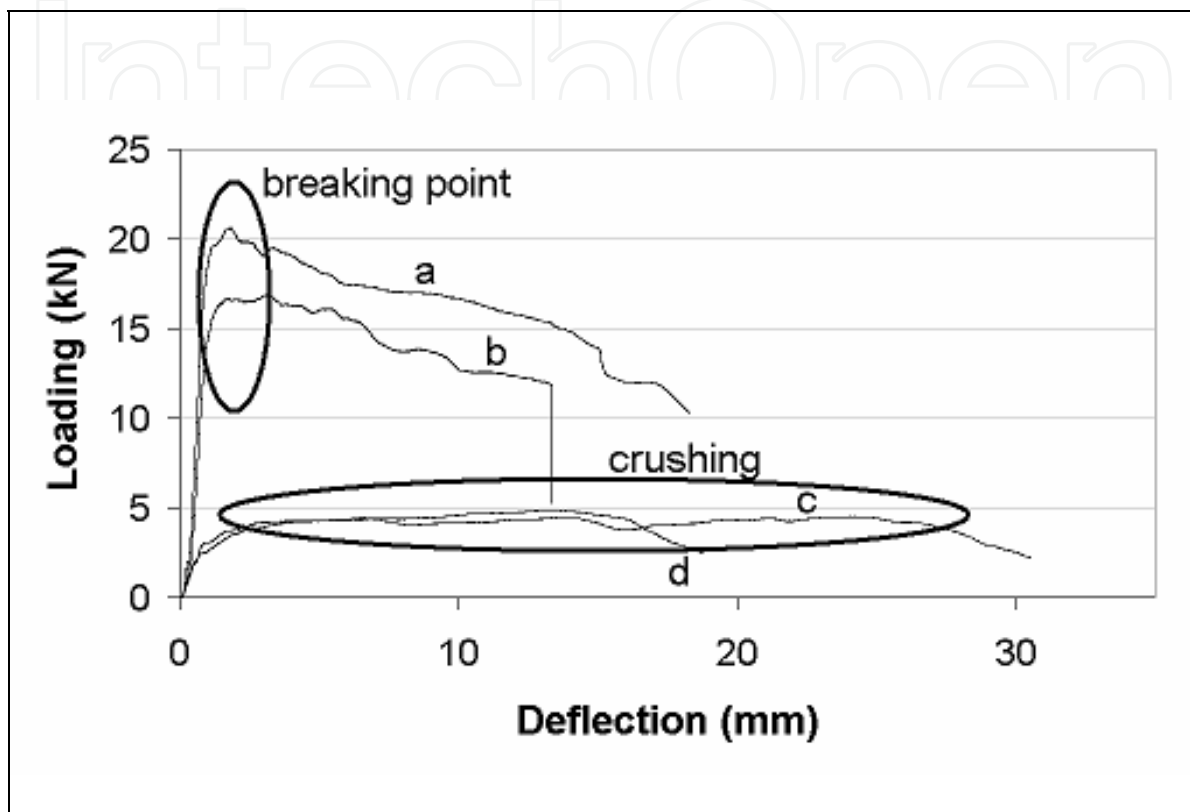


Fig. 10. Compression-breaking curves of pine control specimens (a and b) and specimen subjected to short catalysed treatment (c and d)

3.4 Biological performance

Composites have been subjected to a decay resistance test of 8 weeks against *Gloeophyllum trabeum* and *Coriolus versicolor* for beech samples and *Gloeophyllum trabeum* and *Poria placenta* for pine samples. At the end, control samples have been recognized as nutritive material. Due to their surface acidity, treated samples succeed in repelling the fungi.

4. Industrial application promises

4.1 Perspectives

According to the former sections, a heating catalysed treatment of impregnated wood led under soft conditions leads to a strongly softened material. This softened character remains even under ambient temperature which offers the advantage of a possible moulding in ambient conditions. Then, after a second step of heating, the material recovers its initial stiffness.

Figure 11 gives an overview of some possible applications:

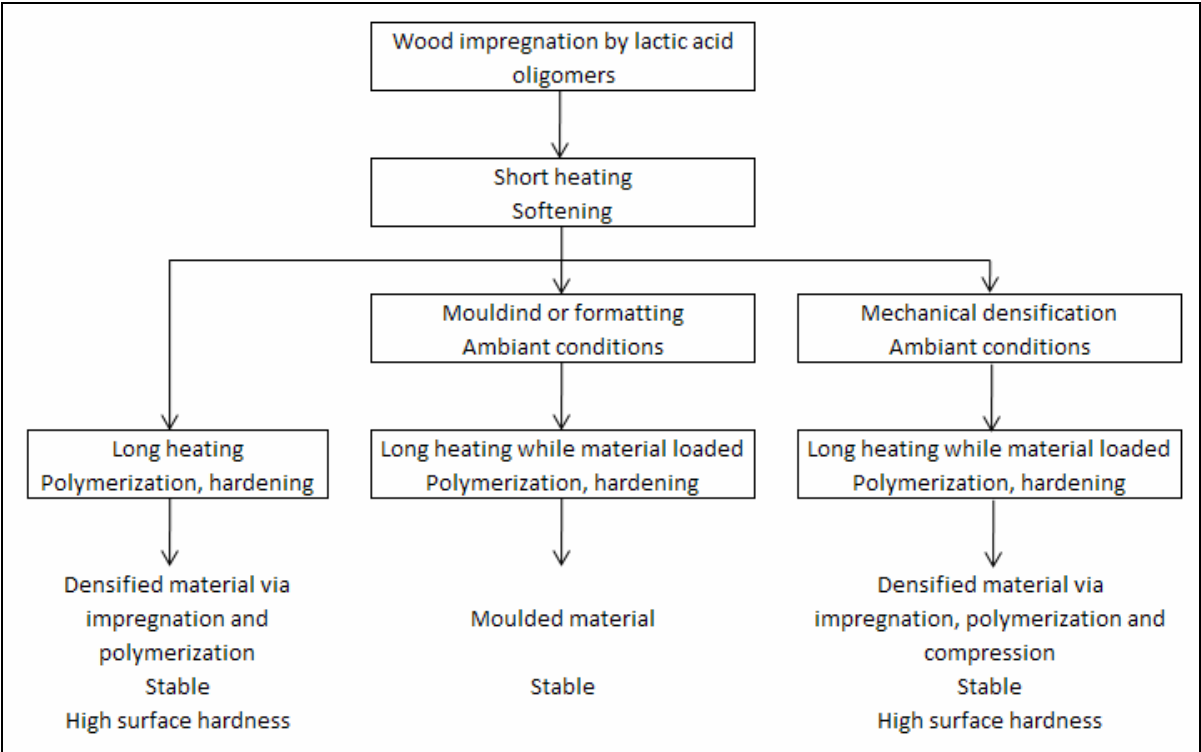


Fig. 11. Applications suggestions

4.2 Wood densification

Wood densification via impregnation and polymerization leads to a competitive material, resistant to biological attack, with high surface hardness and satisfying mechanical properties.

Use of the softened composite to manufacture densified material via impregnation, polymerization and compression would be of high interest in industrial fields as flooring, for instance. Cylindric impregnated samples have been subjected to heating, under loading in a metallic mold. Load has been settled to compress the samples enough to extract the air contained in wood lumens. Compressed and polymerized material consists in cellulosics and lactic acid oligomers only.

Brinell hardness of such composites has been assessed and is summarized in Table 3.

Specimen	HB (MPa)
Beech control	3.9
Compressed beech control	19.9
Non catalysed treated beech sample	5.2
Compressed non catalysed treated beech sample	16.4
Catalysed treated beech sample	4.6
Compressed catalysed treated beech sample	7.8

Table 3. Brinell hardness of compressed composites

A strong increase in surface hardness is noticed when samples are compressed. The increase is even more obvious on control non treated wood. But once subjected to moisture, non treated samples are unstable whereas treated samples shape is fixed.

4.3 Wood moulding

To achieve non treated wood moulding, high temperature and air moisture content are necessary to obtain a plastic behaviour. The advantage of softened composite is its ability to be moulded with low loads, under ambient conditions. Figure 12 shows some radius of curvature applied on softened composite during the next long heating step. Shape is fixed, and the limitation is the fibres decohesion in the radial direction, which could be avoided by use of a suitable mold.

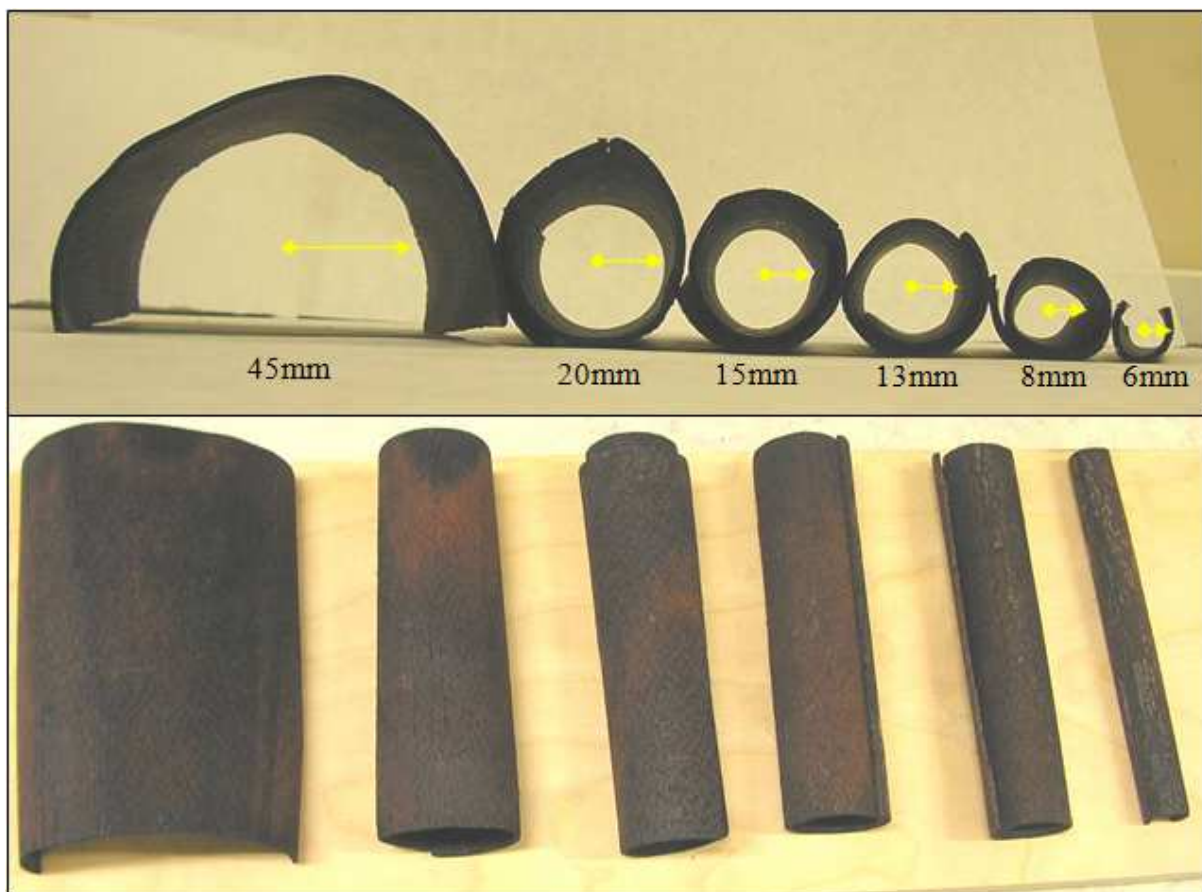


Fig. 12. Moulded and fixed samples

4.4 Further processing

To suppose an industrial development of softened or densified composites, any possible further processing has to be evaluated.

Two polyurethane coatings systems (primer + top-coat), aqueous and solvent based, have been applied on densified composite. Visual inspection is satisfying. Cross-cut (Figure 13) and impact normalized tests show comparable results as those obtained with the same coating systems applied on wood.



Fig. 13. Cross-cut testing carried out on aqueous based coating applied on densified composite

Tools wearing during machining has to be considered as well. Sanding paper is already been recognized as easily spotted when used to sand densified composite samples. Attention must be paid to blades, since surface acidity of densified samples is around pH 3 (wood surface acidity being around pH 6 to 7).

5. Conclusion

Lactic acid oligomers have been used as reinforcement into the lignocellulosic matrix. Without any polymerization catalyst, the densified composite obtained is stable, biologically resistant and mechanically competitive: high density and good hardness results make it suitable for flooring application for instance.

When a polymerization catalyst is added to the oligomers, wood components are damaged. The softened composite obtained can however be hardened again since an extended heating leads to a stable and biologically resistance material. The middle lamella degradation provokes mechanical properties decrease which suggests applications as decorative moulded objects or covering panels rather indoor than outdoor, for instance.

Manufacturing conditions can obviously be optimized to lead to a better composite material: temperature, duration, chemical catalysts, etc.

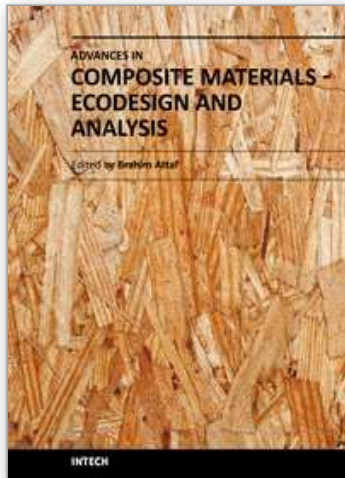
Another field of interest would be either to reinforce wood structure with other bio-polymer molecules, or to use lactic acid oligomers mixture to reinforce other natural matrices as bamboo for instance.

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By adopting the principles of sustainable design and cleaner production, this important book opens a new challenge in the world of composite materials and explores the achieved advancements of specialists in their respective areas of research and innovation. Contributions coming from both spaces of academia and industry were so diversified that the 28 chapters composing the book have been grouped into the following main parts: sustainable materials and ecodesign aspects, composite materials and curing processes, modelling and testing, strength of adhesive joints, characterization and thermal behaviour, all of which provides an invaluable overview of this fascinating subject area. Results achieved from theoretical, numerical and experimental investigations can help designers, manufacturers and suppliers involved with high-tech composite materials to boost competitiveness and innovation productivity.

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